

**CLAIMS**

What is claimed is:

- 1 1. A photovoltaic device, comprising:
  - 2 a nanostructured template made from an n-type first charge transfer-material, the
  - 3 nanostructured template having template elements between about 1 nm and about
  - 4 500 nm in diameter with a template element density of between about  $10^{12}$
  - 5 elements /m<sup>2</sup> and about  $10^{16}$  elements /m<sup>2</sup>;
  - 6 a second charge-transfer material conformally coating one or more walls of the
  - 7 template elements leaving additional space, wherein the first charge-transfer
  - 8 material is n-type and the second charge-transfer is p-type; and
  - 9 a third material in the additional space, wherein the third material is a p-type or
  - 10 conducting material that volumetrically interdigitates with the second charge-
  - 11 transfer material,
  - 12 wherein a lowest unoccupied molecular orbital (LUMO) or conduction band of
  - 13 the first charge-transfer material differs from a LUMO or conduction band of the
  - 14 second charge-transfer material by less than about 1 eV, wherein a light
  - 15 absorbance of at least one charge transfer material is greater than about  $10^3$ /cm at
  - 16 the peak of the absorption spectrum.
- 1 2. The device of claim 1 wherein the third charge-transfer material in the form of
- 2 one or more elongated structures that volumetrically interdigitate with the second
- 3 charge transfer material.
- 1 3. The device of claim 2, further comprising a base electrode and a top electrode,
- 2 wherein the nanostructured template is disposed between the base electrode and
- 3 top electrode.
- 1 4. The device of claim 3, wherein the first charge-transfer material is in electrical
- 2 contact with the base electrode and the third charge-transfer material is in contact
- 3 with the top electrode.

- 1 5. The device of claim 3, further comprising one or more plugs of material at the tips  
2 of the elongated structures, wherein the plugs protect against undesired electrical  
3 contact between the third charge-transfer material and the template and/or base  
4 electrode.
  - 1 6. The device of claim 3 wherein the third charge-transfer material is a transparent  
2 conductive material.
  - 1 7. The device of claim 3 wherein the third charge-transfer material includes an  
2 organic semiconducting material.
  - 1 8. The device of claim 7 wherein the third charge transfer material has a different  
2 light absorption range and/or a different HOMO/LUMO level than the second  
3 charge transfer material.
  - 1 9. The device of claim 2 wherein one or more of the base electrode and top is a  
2 transparent electrode.
  - 1 10. The device of claim 1 wherein the first charge-transfer material is an inorganic  
2 material and the second and third charge-transfer materials are organic materials.
  - 1 11. The device of claim 1 wherein the first charge-transfer material is an electrically  
2 semiconductive or conductive material.
  - 1 12. The device of claim 1 wherein the second charge transfer material coats the  
2 template elements up to a level that is substantially even with an upper surface of  
3 the template.
  - 1 13. The device of claim 1 wherein the first, second, or third charge-transfer material  
2 includes one or more materials from the group of titanium oxide, zinc oxide  
3 (ZnO), copper oxide, copper sulfide, zirconium oxide, lanthanum oxide, niobium  
4 oxide, tungsten oxide, tin oxide, indium tin oxide (ITO), strontium oxide,  
5 calcium/titanium oxide, indium oxide, vanadium oxide, zirconium oxide,  
6 molybdenum oxide, vanadium oxide, strontium oxide, sodium titanate, potassium

7       niobate, silicon, tungsten oxide, cadmium selenide (CdSe), zinc selenide (ZnSe),  
8       cadmium sulfide (CdS), cadmium telluride (CdTe), cadmium selenide (CdSe),  
9       cadmium telluride selenide (CdTeSe), CIS, CISe, CIGS ( $\text{CuInGaSe}_2$ ), copper-  
10      indium selenide, cadmium oxide, or blends or alloys of two or more of these  
11      materials.

- 1     14. The device of claim 1 wherein the first charge-transfer material includes a  
2       transparent conductive oxide.
- 1     15. The device of claim 15 wherein the first charge-transfer material includes  
2       titanium oxide or zinc oxide.
- 1     16. The device of claim 15, wherein the second charge-transfer material is a p-type  
2       semiconducting material.
- 1     17. The device of claim 1, further comprising an interfacial layer disposed between  
2       the first and second charge-transfer materials.
- 1     18. The device of claim 17 wherein the interfacial layer includes one or more  
2       materials chosen from the group of fullerenes, doped fullerenes, functionalized  
3       fullerenes,  $\text{C}_{60}\text{-COOH}$ , doped functionalized fullerenes, azafullerenes,  
4       polymerized fullerenes (doped or undoped), functionalized polymerized fullerenes  
5       (doped or undoped), phenyl- $\text{C}_{61}$ -butyric acid methyl ester (PCBM), carbon  
6       nanotubes, dyes, ruthenium dyes, pigments, organic monomers, oligomers, and  
7       polymers, tetra-hydro-thiophene precursor polymers and derivatives thereof, poly-  
8       phenylene-vinylene and derivatives thereof, conjugated polymers, and/or blends  
9       of these materials.
- 1     19. The device of claim 17 wherein the interfacial layer includes one or more  
2       chemicals that can covalently attach to the first charge-transfer material and  
3       change a surface energy and/or bonding trap-states and/or attach to dangling-  
4       bonds at an exposed surface of the first charge-transfer material and/or introduce a  
5       dipole layer that may increase the efficiency for charge extraction and/or reduce  
6       detrimental charge recombination.

- 1 20. The device of claim 17 wherein the interfacial layer includes C<sub>60</sub> or other  
2 fullerenes functionalized with a carboxylic acid moiety.

1 21. The device of claim 1 wherein the second charge-transfer material includes two or  
2 more complementary charge-transfer materials that are blended together.

1 22. The device of claim 1 wherein the second and third charge-transfer materials are  
2 both organic materials.

1 23. The device of claim 1 wherein the one or more of the second or third charge-  
2 transfer materials includes a material chosen from the group of thiophene-,  
3 fluorine- or aryl-vinyl- based polymers, copolymers or blends, poly(phenylene)  
4 and derivatives thereof, poly(phenylene vinylene) and derivatives thereof, poly(2-  
5 methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV), poly(para-  
6 phenylene vinylene), (PPV), PPV copolymers, poly(thiophene) and derivatives  
7 thereof, poly(3-octylthiophene-2,5,-diyl) regioregular, poly(3-octylthiophene-2,5,-  
8 diyl) regiorandom, poly (3-hexylthiophene) (P3HT), poly(3-hexylthiophene-2,5,-  
9 diyl) regioregular, poly(3-hexylthiophene-2,5-diyl) regiorandom,  
10 poly(thienylenevinylene) and derivatives thereof, poly(isothianaphthene) and  
11 derivatives thereof, tetra-hydro-thiophene precursors and derivatives thereof,  
12 poly-phenylene-vinylene and derivatives, organometallic polymers, polymers  
13 containing perylene units, poly(squaraines) and their derivatives, discotic liquid  
14 crystals polyfluorenes, polyfluorene copolymers, polyfluorene-based copolymers  
15 and blends, polyfluorene-based copolymers co-polymerized and/or blended with  
16 charge transporting compounds , polyfluorene-based copolymers co-polymerized  
17 and/or blended with tri-phenyl-amines and/or derivatives, polyfluorene-based  
18 copolymers co-polymerized and/or blended with light-absorbing compounds,  
19 polyfluorene-based copolymers co-polymerized and/or blended with fused  
20 thiophene rings and derivatives or hetero-atom ring compounds with or without  
21 substituents, pigments, dyes, or fullerenes, and mixtures of these materials.

- 1    24. The device of claim 1, wherein one or more of the second and third charge-  
2 transfer material is a pigment, dye or small molecule chosen from the group of  
3 organic pigments or dyes, azo-dyes having azo chromophores (-N=N-) linking  
4 aromatic groups, phthalocyanines including metal-free phthalocyanine; (HPc),  
5 Zinc phthalocyanine (ZnPc), Copper phthalocyanine (CuPc), perylenes,  
6 naphthalocyanines, squaraines, merocyanines and their respective derivatives,  
7 poly(silanes), poly(germinates), 2,9-Di(pent-3-yl)-anthra[2,1,9-def:6,5,10-  
8 d'e'f]diisoquinoline-1,3,8,10-tetrone, and 2,9-Bis-(1-hexyl-hept-1-yl)-  
9 anthra[2,1,9-def:6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetrone, pentacene and/or  
10 pentacene precursors, and mixtures of two or more of these materials.
- 1    25. The device of claim 1 wherein one or more of the second or third charge-transfer  
2 materials includes one or more materials chosen from the group of fullerenes,  
3 doped fullerenes, functionalized fullerenes, doped functionalized fullerenes,  
4 azafullerenes, polymerized fullerenes (doped or undoped), functionalized  
5 polymerized fullerenes (doped or undoped), carbon nanotubes, dyes, ruthenium  
6 dyes, pigments, organic monomers, oligomers, and polymers, tetra-hydro-  
7 thiophene precursor polymers and derivatives thereof, poly-phenylene-vinylene  
8 and derivatives thereof, conjugated polymers, and mixture of these materials.
- 1    26. The device of claim 1 wherein the template elements are in the form of hollow  
2 tubes that protrude from the template with spaces between the sidewalls of the  
3 tubes.
- 1    27. The device of claim 1 wherein the third charge transfer material includes one or  
2 more transparent conducting materials.
- 1    28. The device of claim 27 wherein the one or more transparent conducting materials  
2 include PEDOT, PEDOT doped with a dopant PEDOT doped with polystyrene  
3 sulfonic acid (PSS), doped 2,2'7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-  
4 9,9'-spirobifluorene (doped *spiro-MeOTAD*), doped spiro-MeOTAD, polyaniline

- 5       doped with a dopant, and/or polyaniline doped with a dopant polystyrene sulfonic  
6       acid (PSS)).
- 1   29. The device of claim 27 wherein the one or more transparent conducting materials  
2       conformally coat and interdigitate into the second charge transfer material.
- 1   30. The device of claim 1 wherein the second and third charge-transfer materials are  
2       both inorganic materials.
- 1   31. The device of claim 1 wherein the second and third charge transfer materials are  
2       the same material.
- 1   32. A photovoltaic device, comprising:  
2       a base electrode;  
3       a top electrode;  
4       a nanostructured template disposed between the base electrode and top electrode,  
5       wherein the nanostructured template is made of an n-type material, the  
6       nanostructured template having template elements between about 1 nm and about  
7       500 nm in diameter with a template element density of between about  $10^{12}$   
8       elements /m<sup>2</sup> and about  $10^{16}$  elements /m<sup>2</sup>;  
9       a p-type material coating on one or more walls of the template elements in a way  
10      that leaves additional space; and  
11      a charge-transfer material in the additional space, wherein the charge-transfer  
12      material volumetrically interdigitates with the p-type material.
- 1   33. A method for making a photovoltaic device, comprising the steps of:  
2       forming a nanostructured template from a first charge-transfer material, the  
3       nanostructured template having template elements between about 1 nm and about  
4       500 nm in diameter with a template element density of between about  $10^{12}$   
5       elements /m<sup>2</sup> and about  $10^{16}$  elements /m<sup>2</sup>;  
6       coating one or more walls of the template elements with a second charge-transfer  
7       material in a way that leaves additional space, wherein the second charge-transfer  
8       material has complementary charge-transfer properties with respect to the first

- 9           charge-transfer material; and  
10          filling the additional space with a third charge-transfer material.
- 1   34.   The method of claim 33 wherein the first charge-transfer material includes  
2           titanium oxide or zinc oxide.
- 1   35.   The method of claim 33 wherein forming a nanostructured template includes  
2           anodizing a layer of metal.
- 1   36.   The method of claim 33 further comprising disposing an interfacial layer between  
2           the second and third charge transfer materials.
- 1   37.   The method of claim 33 wherein the third charge-transfer material includes one or  
2           more elongated structures that interdigitate with the second charge transfer  
3           material.
- 1   38.   The method of claim 37 further comprising capping one or more tips of the  
2           elongated structures with a short-proofing material.
- 1   39.   The method of claim 33 wherein coating one or more walls of the template  
2           elements with the second charge-transfer material includes depositing the second  
3           charge transfer material on the walls of the nanostructured template.
- 1   40.   The method of claim 39 wherein depositing the second charge transfer material on  
2           the walls of the nanostructured template includes the use of a technique selected  
3           from the group of electrochemical deposition, electroless (chemical bath)  
4           deposition, layer-by-layer deposition, evaporation, sputtering, plating, ion-plating,  
5           molecular beam epitaxy, and sol-gel based deposition, spray pyrolysis, vapor-  
6           phase deposition, solvent vapor deposition, atomic layer deposition, plasma-  
7           enhanced atomic layer deposition, atomic vapor deposition, metal-organic vapor  
8           phase deposition, metal-organic-vapor-phase epitaxy, chemical vapor deposition,  
9           metal-organic chemical vapor deposition, plasma enhanced chemical vapor  
10           deposition, self-assembly, electro-static self-assembly, melt-filling/coating  
11           electro-deposition, electro-plating, ion-plating, or liquid phase deposition.

- 1    41. The method of claim 33 wherein filling the additional space with the third charge  
2 transfer material includes depositing the third charge transfer material by a  
3 technique selected from the group of electrochemical deposition, electroless  
4 (chemical bath) deposition, layer-by-layer deposition, evaporation, sputtering,  
5 plating, ion-plating, molecular beam epitaxy, and sol-gel based deposition, spray  
6 pyrolysis, vapor-phase deposition, solvent vapor deposition, atomic layer  
7 deposition, plasma-enhanced atomic layer deposition, atomic vapor deposition,  
8 metal-organic vapor phase deposition, metal-organic-vapor-phase epitaxy,  
9 chemical vapor deposition, metal-organic chemical vapor deposition, plasma  
10 enhanced chemical vapor deposition, self-assembly, electro-static self-assembly,  
11 melt-filling/coating electro-deposition, electro-plating, ion-plating, or liquid phase  
12 deposition.
  
- 1    42. The method of claim 33 wherein the third charge transfer material includes one or  
2 more transparent conducting materials.
  
- 1    43. The method of claim 42 wherein the one or more transparent conducting materials  
2 include PEDOT, PEDOT doped with a dopant PEDOT doped with polystyrene  
3 sulfonic acid (PSS), doped 2,2'7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-  
4 9,9'-spirobifluorene (doped *spiro-MeOTAD*), doped spiro-MeOTAD, polyaniline  
5 doped with a dopant, and/or polyaniline doped with polystyrene sulfonic acid  
6 (PSS)).
  
- 1    44. The method of claim 42 wherein the one or more transparent conducting materials  
2 conformally coat and interdigitate into the second charge transfer material.
  
- 1    45. The method of claim 44 wherein the one or more transparent conducting materials  
2 include PEDOT, PEDOT doped with a dopant PEDOT doped with polystyrene  
3 sulfonic acid (PSS), doped 2,2'7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-  
4 9,9'-spirobifluorene (doped *spiro-MeOTAD*), polyaniline doped with a dopant,  
5 and/or polyaniline doped with polystyrene sulfonic acid (PSS)).